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THE ALKALI METAL REDUCTION OF PYRENE - STRUCTURAL AND PREPARATIVE ASPECTS

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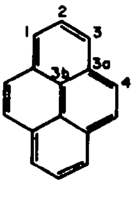
Abstract. Reduction of pyrene with alkali metals yields the corresponding dianion salts. The solvent, counterion and temperature must be carefully selected since side reactions such as protonation (e.g. in liquid ammonia) or cleavage of the etheral solvent occur readily. Moreover, the spectroscopic characterization of the dianion is complicated by rapid electron transfer processes. There is no experimental evidence for distorted dianion structures or for further reduction of pyrene toward a tetraanion. Knowledge of the ionic π-structures is essential for an understanding of reductive alkylation processes.

1. Introduction. - Via careful alkali metal reduction of unsaturated hydrocarbons we have recently succeeded in preparing and spectroscopically characterizing the metal salts of dianionic [1-3] and tetraanionic [4-6] π-systems with intact molecular framework. These species represent most useful model compounds for structural studies concerned with π-charge distribution,[5,7] ion pairing,[8] and ring current effects.[9,10] A challenging example is the pyrene molecule 1 whose dianion 1^{2-} we have generated as dilithium salt.[11] It appears from NMR data that 1^{2-} possesses D_{2h} symmetry and is strongly paratropic.



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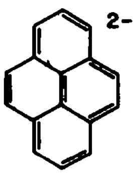
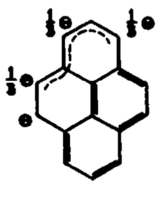


1^{2-}

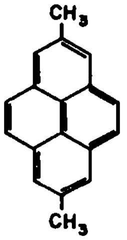


$(1^{2-})^*$

In contrast to our findings the pyrene dianion has recently been claimed to adopt the distorted structure $(1^{2-})^*$.[12] Further reduction with sodium in tetrahydrofuran (THF) at room temperature has been reported to give a tetraanionic derivative.[13]

We provide evidence here, which convincingly supports our structural assignments. Incorrect conclusions given in the literature stem from the (overlooked) fact that the reduction of pyrene sensitively depends on the reaction conditions and may be accompanied by side reactions.

2. Results. 2.1. Reduction of 1 with Sodium or Lithium in Tetrahydrofuran (THF) at Low Temperatures. Reduction of 1 (sodium or lithium, THF, -80°C) yields the radical anion $1^{\cdot-}$ which is detected by its well-known ESR signal.[14] The primary diamagnetic product which is seen in the ^{1}H NMR spectrum can be identified as the monoanion $(1\text{-H})^-$. Particularly characteristic in the spectrum of the protonation product $(1\text{-H})^-/\text{Li}^+$ (see Figure 1) is the resonance at δ =4.17 which is due to two protons and which can be assigned to H-1 and H-1'. Homonuclear decoupling helps to identify the signal of H-2 at δ=4.31 and to assign the other resonances.



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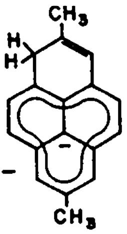
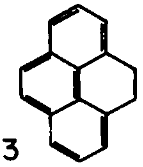


$(2\text{-H})^-$



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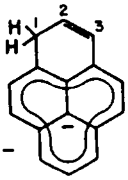


$(1\text{-H})^-$

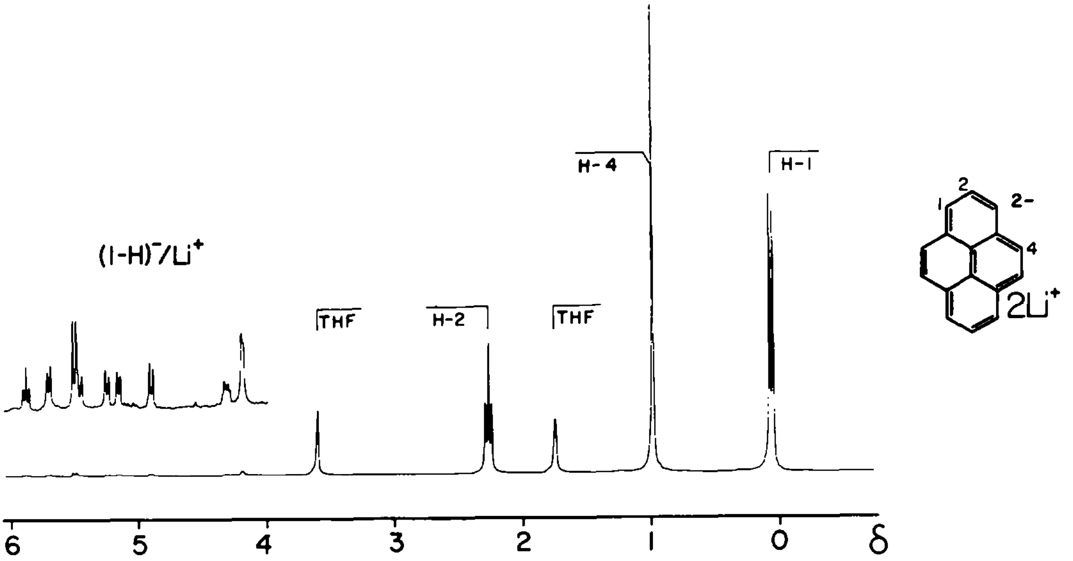


Figure 1. ^1H NMR spectrum [300 MHz, THF-D_8, -40°C] of a sample containing $1^{2-}/2Li^+$ and a trace of $(1\text{-}H)^-/Li^+$. The sample has been prepared from a 0.02 M solution of 1 by reduction for 2h.

The spectra of $(1\text{-}H)^-/Li^+$ and $(1\text{-}H)^-/Na^+$, thus, leave no doubt as to the site of protonation (see Figures 1 and 2).

This conclusion is supported by the results obtained when 2,7-dimethylpyrene (2) is reduced as described above: the hydrogens at positions 1,3,6 and 8 of the original pyrene moiety resonate as a singlet. Lowering of the symmetry upon formation of $(2\text{-}H)^-/Li^+$ gives rise to four singlets with relative intensity 1:1:1:2, one of which (2H) appearing at significantly higher field.

Prolonged metal contact of the pyrene sample gives rise to the deep blue solution of the dianion (sodium or lithium salt). The 3 signals in the ^1H [singlet (4H), doublet (4H), triplet (2H)] and the 5 signals in the ^{13}C NMR spectrum of $1^{2-}/2Li^+$ reveal the intact D_{2h} symmetry of the π-system (see Table). The assignment of the ^{13}C resonances follows from selective ^1H decoupling experiments. The quarternary carbons are identified from their relative intensities. In addition to the ^1H and ^{13}C resonances the dianion salt $1^{2-}/2Li^+$ gives rise to a single absorption of the ^7Li counterions at δ=5.45.

In the following the behaviour of the sodium and lithium systems will be treated separately and the differences emphasized.

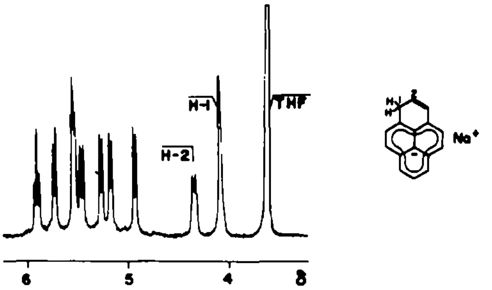


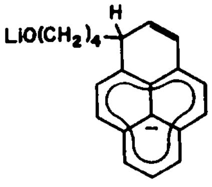
Figure 2. ^1H NMR spectrum [300 MHz, THF-D_8, 25°C] of $(1\text{-}H)^-/Na^+$.

It is obvious from ESR spectroscopy that the final solution of $1^{2-}/2Na^+$ no longer contains the radical anion $1^{\dot{-}}$. However, a small amount of a secondary paramagnetic product is observed ESR spectroscopically and can be identified from its hyperfine coupling constants [in mT: 0.467(2H), 0.329(2H), 0.293 (2H), 0.054(4H), < 0.01(2H)] as the radical anion of the dihydropyrene species 3. Warming of the solution to room temperature does afford the radical anion $1^{\dot{-}}$ whose ESR signal increases with time. After standing at -80°C for ca. 24 h the signal of $1^{\dot{-}}$ disappears. After standing at room temperature for several days the radical signal also disappears. The ESR absorption of the secondary radical anion $3^{\cdot-}$ is unaffected by both the warming and recooling procedure.

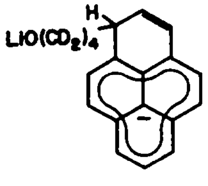
Complementary observations can be made when monitoring the effect of temperature by ^{1}H NMR spectroscopy. On warming to temperatures above -70°C the resonances of $1^{2-}/2Na^+$ suffer from increasing line broadening until at room temperature the signals disappear in the noise (see Figure 3). The only reduction product detectable in the NMR at room temperature is the monoanion $(1\text{-H})^-/Na^+$. The lineshape effect appears to be reversible and even after warming of the sample to +80°C for 12 h the low temperature NMR measurement indicates the original concentration of $1^{2-}/2Na^+$. As in the case of the sodium salt the ^{1}H NMR resonances of the lithium salt $1^{2-}/2Li^+$ broaden upon warming, the broadening effect starting at much higher temperatures (see Figure 3). Two differences between the sodium and lithium reduction are obvious:

- the secondary radical anion $3^{\cdot-}$ is not observed during the lithium reduction;
- when warming the dianion solution of $1^{2-}/2Li^+$ to room temperature yet another secondary product, $(4\text{-D}_8)^-/Li^+$, is observed in the NMR and the colour changes from blue to red.

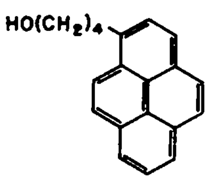
From its NMR spectra $(4\text{-D}_8)^-/Li^+$ appears to be very similar, but not identical with $(1\text{-H})^-/Li^+$. The formation of this compound is irreversible and implies the incorporation of a solvent molecule into the pyrene moiety.



4^-



$(4\text{-D}_8)^-$



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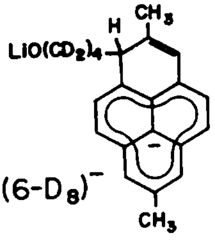


$(6\text{-D}_8)^-$

The structure proof for $(4\text{-D}_8)^-/Li^+$ and $4^-/Li^+$, respectively, rests upon ^{1}H and ^{13}C NMR spectroscopic evidence (see below), the observation of two ^{7}Li resonances of $(4\text{-D}_8)^-/Li^+$ at δ=0.43 and δ=-0.33, as well as quenching experiments: the anion $4^-/Li^+$ is reductively prepared in "normal", i.e. non-deuterated THF (see Experimental Part), protonated by methanol and then reoxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The spectroscopic data for the newly formed pyrene species 5 are given in the Table.

Species $(4\text{-D}_8)^-/Li^+$ exists in two closely related diastereomeric forms. This follows from the ^{1}H NMR signals for H-2 recorded at 300 MHz and 400 MHz under decoupling of H-1 or H-3. Further in the ^{13}C NMR spectrum of $(4\text{-D}_8)^-/Li^+$ (see Figure 4) 13 signals out of 20 (the number expected from the constitutional formula) appear to be doubled with chemical shift differences $\Delta\delta$ between 0.02 and 0.23 ppm.

The ^{1}H NMR spectrum of $(4\text{-D}_8)^-/Li^+$ (300 MHz) shows 7 separate multiplets with relative intensity 2:3:1:1:1:1:1. The assignment is based on decoupling experiments and supported by a comparison with the related species $(6\text{-D}_8)^-/Li^+$ obtained upon decomposition of the dimethylpyrene 2. However, an unequivocal assignment can only be made for the resonances of H-1, H-2, H-3 and H-7. The signals of H-6 and H-8 were not distinguished from each other but are recognizable relative to those of the remaining ones. The same holds true for the case of H-4, H-5, H-9 and H-10.

The SCF-π-charge densities have been calculated for the vinyl phenalene moiety occuring in both $(1\text{-H})^-$ and $(4\text{-D}_8)^-$. Assuming that the sequence of the ^{1}H resonances follows the relative π-charge densities,[5,7] one arrives at the assignment given in the Table.

The most significant outcome from the ^{13}C NMR spectrum of $(4\text{-D}_8)^-$ is the occurrence of the aliphatic resonance of C-1 (C-methin) and of the aliphatic resonances of the side chain. The assignment of the olefinic signals makes use of "off-resonance" and selective ^{1}H decoupling experiments. The assignment of C-2 and C-3 is compelling. A complicating factor is the overlap of 3 proton signals at ca. δ=5.7 and of 2 signals at δ=5.98. In those cases the assignment is based on a correlation with the corresponding π-charge densities. Among the signals for quaternary carbons two appear at significantly higher field than the others. From the relevant q_{π}-values these are assigned as being due to C-3a and C-10a.

Table. ^{1}H and ^{13}C NMR chemical shifts [a] of $\underline{1}^{2-}/2Li^{+}$, $\underline{1}^{2-}/2Na^{+}$, $(\underline{1}\text{-}H)^{-}/Li^{+}$, $(\underline{1}\text{-}H)^{-}/Na^{+}$, $(\underline{4}\text{-}D_8)^{-}/Li^{+}$, $(\underline{2}\text{-}H)^{-}/Li^{+}$, $(\underline{6}\text{-}D_8)^{-}/Li^{+}$ and of $\underline{5}$.

[a] The ionic species have been measured in THF-D_8, the ^{13}C NMR spectrum of $(\underline{1}\text{-}H)^{-}Li^{+}$ in THF/NH_3 (5:1) and of $\underline{5}$ in CD_2Cl_2.

C-atoms			1	2	3	4	5	6	7	8	9	10
$\underline{1}^{2-}/2Li^{+}$	^{1}H	-40°C	0.02	2.20		0.93						
$\underline{1}^{2-}/2Na^{+}$	^{1}H	-80°C	-0.73	1.69		0.24						
$\underline{1}^{2-}/2Li^{+}$	^{13}C	-40°C	92.0	139.8		107.3						
$(\underline{4}\text{-}D_8)^{-}Li^{+}$	^{1}H	+25°C	3.81	4.49 4.53	5.65	5.98	5.71	5.33	5.98	5.43	5.09	5.71
$(\underline{4}\text{-}D_8)^{-}Li^{+}$	^{13}C	+25°C	42.99 43.04	111.87 112.03	128.25 128.31	127.10 127.20	108.40	104.74 104.80	126.39	105.34	101.70 101.72	126.85
$(\underline{6}\text{-}D_8)^{-}Li^{+}$	^{1}H	-30°C	3.73		5.55	5.97	5.61	5.20		5.28	5.10	5.71
$(\underline{1}\text{-}H)^{-}Li^{+}$	^{1}H	-30°C	4.17	4.31	5.44	5.69	5.48	5.13	5.87	5.29	4.88	5.48
$(\underline{2}\text{-}H)^{-}Li^{+}$	^{1}H	-30°C	4.0		5.37	5.82	5.51	5.08		5.14	4.95	5.57
$(\underline{1}\text{-}H)^{-}Na^{+}$	^{1}H	+25°C	4.05	4.32	5.43	5.69	5.51	5.14	5.86	5.24	4.91	5.51
C-atoms			**3a**	**5a**	**8a**	**10a**	**3b**	**5b**	**1a**	**1b**	**1c**	**1d**
$\underline{1}^{2-}/2Li^{+}$	^{13}C		147.6				160.1					
$(\underline{4}\text{-}D_8)^{-}Li^{+}$	^{13}C		109.44 109.47	140.65	136.71 136.74	112.32 112.41	142.08	136.15	42.80	37.15	20.38	64.15

^{1}H NMR chemical shifts of $\underline{5}$ in $CDCl_3$ at 25°C: δ=7.88-8.32 (H-Phenyl); 3.37 (H-a); 1.92 (H-b); 1.72 (H-c); 3.66 (H-d); 1.43(H-e).

^{13}C chemical shifts of $(\underline{1}\text{-}H)^{-}Li^{+}$ in THF/NH_3 (5:1) at -40°C: δ=34.0(C-1); 100.7; 104.7; 104.7; 106.6(q.); 107.9; 108.3(q.); 109.3; 126.5; 126.8; 126.8; 129.4; 136.3(q.);138.0(q.); 140.7(q.); 143.1(q.).

2.2. Reduction of 1 with Sodium or Lithium in THF at Room Temperature. As expected from the above results the reduction at room temperature does not allow the NMR spectroscopic detection of the pyrene dianion. Upon reduction with sodium one observes signals of $(\underline{1}\text{-}H)^{-}/Na^{+}$ and upon reduction with lithium those of $(\underline{1}\text{-}H)^{-}/Li^{+}$ and $(\underline{4}\text{-}D_8)^{-}/Li^{+}$.

ESR spectroscopic monitoring of the reduction is now more revealing. In both cases one detects the signals of the radical anions $\underline{1}^{\dot{-}}/Na^{+}$ and $\underline{1}^{\dot{-}}/Li^{+}$. The signals of $\underline{1}^{\dot{-}}/Na^{+}$ decreases in intensity and, after 6 days of metal contact, disappear in the baseline. Even after such a long reaction time irradiation of the sample with visible light gives rise to the ESR absorption of $\underline{1}^{\dot{-}}/Na^{+}$ as a result of photooxidation of $\underline{1}^{2-}/2Na^{+}$.[15] The ESR signal of the radical anion disappears upon renewed metal contact.

In the course of the lithium reduction the ESR signal of $\underline{1}^{\dot{-}}/Li^{+}$ does not totally disappear even after 7 days of metal contact. However, the signal of $\underline{1}^{\dot{-}}/Li^{+}$ increases upon photolysis. The ESR absorption of $\underline{1}^{\dot{-}}/Li^{+}$ does disappear after reduction at 100°C. Subsequent photolysis does not give rise to the signal of $\underline{1}^{\dot{-}}/Li^{+}$.

Two additional experimental results must be mentioned which are important for the formation of the "hydroproduct" $(\underline{1}\text{-}H)^{-}$. - When working in deuterated THF one does not observe the incorporation of deuterium. The same finding is made during the ESR spectroscopic description of $\underline{3}^{\dot{-}}$. - Under the given experimental conditions formation of

(1-H)$^-$ is only significant when starting out from dilute solutions (e.g. 0.02 M). When working with more concentrated solutions (e.g. 0.5 M) the amount of (1-H)$^-$ formed is negligible. The same result appears upon working with a scrupulously dried solvent system. Thereby, the evacuated NMR tube is dried with a flame and the solvent distilled in from a short side arm which contains a THF solution of the pyrene dianion.

2.3. Reduction of 1 with Potassium in Dimethoxyethane at Low Temperatures. The originally observed ESR spectrum of $1^{\cdot-}/K^+$ disappears after 2 h of metal contact without noticeable formation of a secondary paramagnetic product. Prolonged reduction produces the singlet signal of the solvated electron. Photolysis of the sample gives rise to the radical anion signal; however, the photooxidation is reversible since the ESR signal immediately disappears after switching off the lamp.

2.4. Reduction of 1 in Etheral Solvents Containing Liquid Ammonia. A solution of 1 in THF/NH_3 (5:1) maintains a red colour from -80°C to +25°C.

The ESR signal of the radical anion disappears when the tube is allowed to stand for several days. At this stage the photolysis fails to produce the spectrum of $1^{\cdot-}$.

Related information comes from monitoring the reduction by ^{13}C NMR spectroscopy (see Figure 5). The initially observed resonances are those of the protonated species (1-H)$^-$. The triplet absorption from C-1 (off-resonance decoupled ^{13}C NMR) is particularly revealing. The ^1H NMR spectrum recorded in THF-D_8/ND_3 (5:1) is similar to the one of (1-H)$^-$ in THF with the exception that the relative signal intensity of H-1 and H-2 is now 1:1.

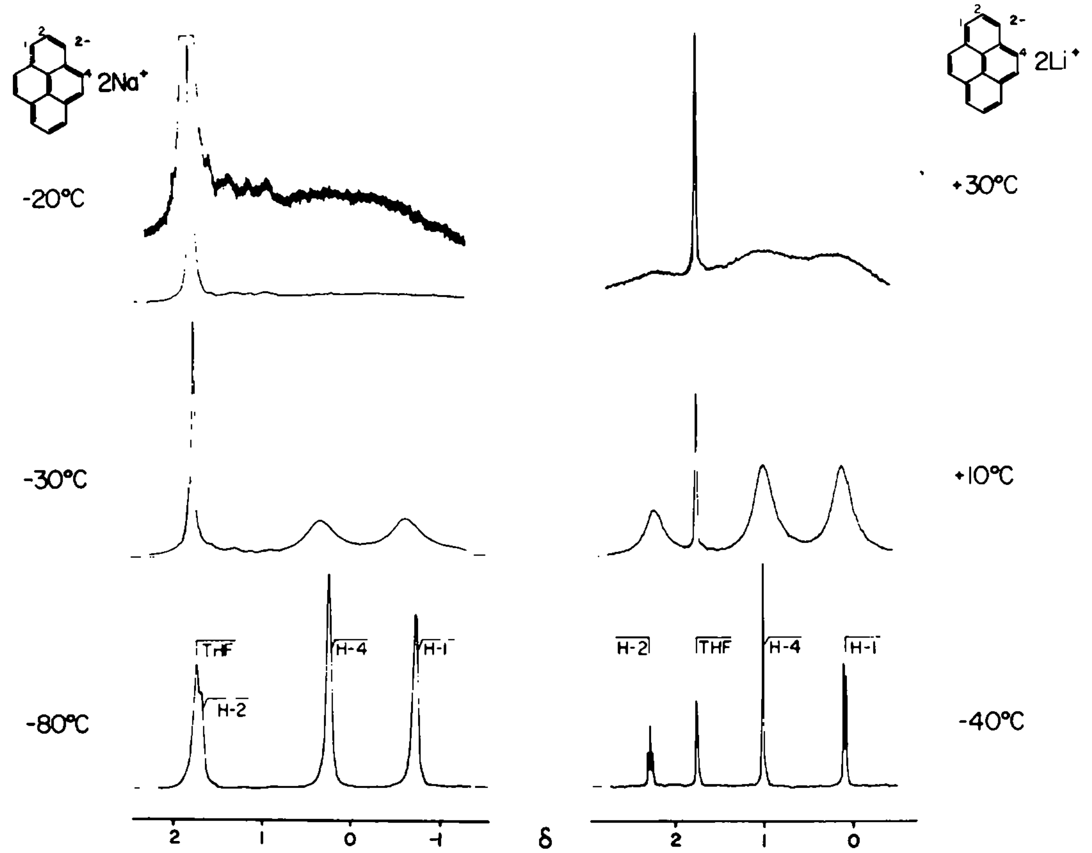


Figure 3. ^1H NMR spectra [300 MHz,THF-D_8] of $1^{2-}/2Li^+$ and $1^{2-}/2Na^+$ at different temperatures. (It should be noted that the appearance of the spectra depends on the experimental conditions such as concentration and reduction time.)

3. Discussion. 3.1. Structures of Ionic Pyrene Species Produced under Different Reduction Conditions. Reduction of pyrene at low temperatures with either lithium, sodium or potassium provides the dianion $\underline{1}^{2-}$ as main product. The existence of $\underline{1}^{2-}$ can easily be deduced from the well-resolved ^{1}H, ^{13}C and (in the case of $\underline{1}^{2-}/2Li^{+}$) ^{7}Li NMR spectra. Additional evidence for the dianion formation can be taken from quenching experiments (see below) and from the fact that irradiation of the blue dianion solution with visible light produces the radical anion $\underline{1}^{\dot{-}}$ via photooxidation. Moreover, it can be inferred from the number of ^{1}H, ^{13}C and ^{7}Li resonances that $\underline{1}^{2-}$ possesses an intact molecular framework with D_{2h} symmetry. These results are in accord with our early structural assignments,[11] but do not support the distorted structure $(\underline{1}^{2-})*$ suggested previously.[12]

The NMR signals of the dianion are not affected upon prolonged metal contact and the reduction with potassium in DME produces the ESR signal of the solvated electron after disappearance of the radical anion signal. There seems to be no indication from the low-temperature experiments that the reduction proceeds beyond the dianion state toward a tri- or tetraanion.[13]

It is important for an interpretation of the pyrene reduction that the NMR spectra of the dianion be recorded at low temperatures (see Figure 3). At elevated temperatures (see Section 2) one observes a progressive line broadening until at room temperature the NMR signals of e.g. $\underline{1}^{2-}/2Na^{+}$ disappear in the noise. The line broadening effect observed upon a temperature change of the sample of e.g. $\underline{1}^{2-}/2Na^{+}$ is reversible. We conclude that $\underline{1}^{2-}/2Na^{+}$ can be kept at room temperature in etheral solvents without serious decomposition.

The severe broadening of the NMR signals can be ascribed to a rapid electron exchange between the dianion $\underline{1}^{2-}$ and the radical anion $\underline{1}^{\dot{-}}$ which is known to be present in the solution. The origin of the radical anion formation upon warming of the dianion sample is not perfectly clear. One might assume that at low temperatures $\underline{1}^{\dot{-}}$ is in equilibrium with a diamagnetic dimer (or higher aggregates) which is cleaved again at higher temperatures. As an additional possibility one could consider a partial reoxidation of the dianion upon warming (e.g. via electron transfer to the solvent, see below).

What one observes in the NMR spectra at room temperature are the resonances of the monoanion $(\underline{1}\text{-H})^{-}$. It follows from the relative signal intensities of $(\underline{1}\text{-H})^{-}$ and $\underline{1}^{2-}$ (taken at low temperature, see Figure 1) that the monoanion is a minor side product. The spectra that must be assigned to $(\underline{1}\text{-H})^{-}$ are very similar to those found for the distorted dianion structure $(\underline{1}^{2-})*$ [12] or the tetraanion structure of pyrene.[13]

The formation of $(\underline{1}\text{-H})^{-}$ can be explained by the protonation of the dianion or of the radical anion. It is clear that the solvent (THF) is not the proton source since working in deuterated THF does not lead to an incorporation of deuterium. The same is true for the paramagnetic side product $3^{\dot{-}}$ which is observed in the ESR.

It is known, on the other hand, that pyrene can be lithiated with n-butyllithium at room temperature.[16] In a similar fashion the alkali metal salt $\underline{1}^{2-}/2Li^{+}$ might serve as a metalating agent and metalate neutral pyrene being itself transformed into the monoanion $(\underline{1}\text{-H})^{-}$. As an alternative possibility the proton could be provided by traces of water present in the etheral solution. The latter explanation is strongly supported by the fact that the relative amount of the monoanion decreases with increasing concentration of the starting material. During the lithium reduction of a 0.5 M pyrene solution the amount of $(\underline{1}\text{-H})^{-}$ is negligible. We have also succeeded in surpressing the formation of $(\underline{1}\text{-H})^{-}$ by working in more dilute, but carefully dried THF solutions (see Section 2).

Upon the reduction of pyrene with lithium in THF one observes yet another side reaction since reducing the sample at room temperature or warming the dianion solution to room temperature gives rise to the species $(\underline{4}\text{-}D_8)^{-}/Li^{+}$ (in THF-D_8) or $\underline{4}^{-}/Li^{+}$ (in THF), respectively. The structure proof of the products rests upon the spectroscopic and chemical evidence given in Section 2.

Clearly, the above side reaction proceeds via the attack of the reduction product upon the solvent molecule. The cleavage of the THF-ring by organometallic compounds RLi has been well documented.[16] Thereby, the five-membered ring yields the enolate of acetaldehyde plus ethylene which then inserts into the RLi bond.[17] Such a process has also been invoked for the decomposition of ions derived from phenanthrene in THF at room temperature.[18]

In contrast, we observe that the C-O-cleavage of the heterocyclic ring is followed by the incorporation of a - $(CH_2)_4O$ - moiety into the pyrene system. Related examples of solvent decomposition by organometal species have been reported in the literature.[19] The ring opening to afford $\underline{4}^-/Li^+$ could be formulated as a nucleophilic substitution process or as involving an electron transfer. We recall that upon warming the pure (i.e. free of $\underline{1}^{\cdot-}$) dianion solution one ESR spectroscopically detects the radical anion $\underline{1}^{\cdot-}$ which at low temperatures (without further metal contact) disappears only after several hours. In this respect it is also important that the secondary reactions do not proceed quantitatively. Photolysis of the above samples (containing $\underline{4}^-/Li^+$) generates the pyrene radical anion and the sample from which one isolates the alcohol $\underline{5}$ contains appreciable amounts of pyrene.

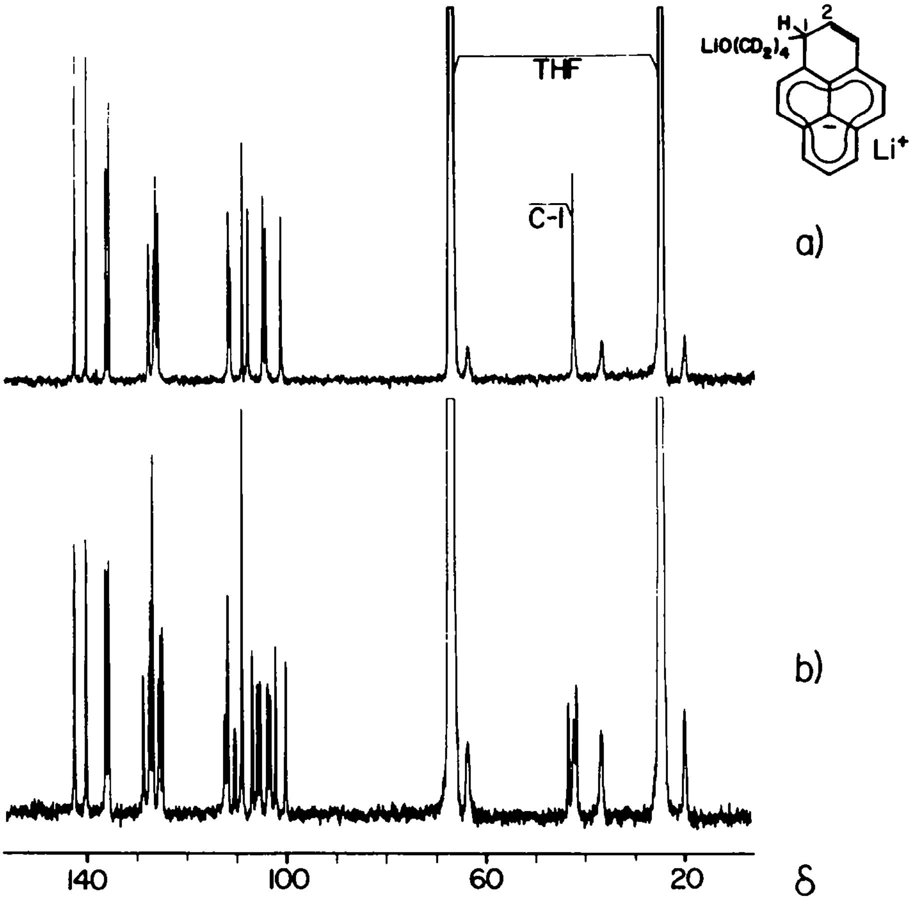


Figure 4. ^{13}C NMR spectra [75.5 MHz, THF-D_8, 25°C; a) decoupled, b) non-decoupled] of $(\underline{4}-D_8)^-/Li^+$. The sample has been prepared as described in the text.

It has been concluded from the highly resolved ^1H and ^{13}C NMR spectra that $(\underline{4}-D_8)^-/Li^+$ exists in two closely related diastereomeric forms with almost equal concentration. The origin of this isomerism (constitutional isomerism can be excluded due to the nearly identical chemical shifts) is not clear. A possible explanation can assume that the substituted six-membered ring of $(\underline{4}-D_8)^-/Li^+$ adopts a non-planar geometry with the side chain in either an axial or equatorial position. A similar observation has been made for radical anions derived from cyclohexadienyl systems.[20] The fact that the vicinal coupling constant of H-1 and H-2 is more or less the same in both isomers (4.5 and 4.7 Hz) seems to indicate a planar structure, probably with different ion pair structures (including e.g. a syn- or anti-arrangement of the $-(CD_2)_4OLi$ - unit and the lithium counterion of the phenalene system).

An important finding is made when the reduction of pyrene is performed in solutions containing liquid ammonia. The ^1H NMR and ^{13}C NMR spectra taken shortly after the pyrene has been added to the solution (see Figure 5 and Section 2) indicate that only the monoanion $(\underline{1}\text{-H})^-$ is present. One concludes that under these experimental conditions the pyrene dianion does not persist, but is rapidly protonated by the ammonia. Monitoring the reduction by ESR spectroscopy reveals that the radical anion can be detected in the THF/NH_3-solution. Its ESR signal disappears only after standing for several days. That this is not due to dianion formation can be deduced from the photolysis of the final solution which does not afford $\underline{1}^{\dot{-}}$.

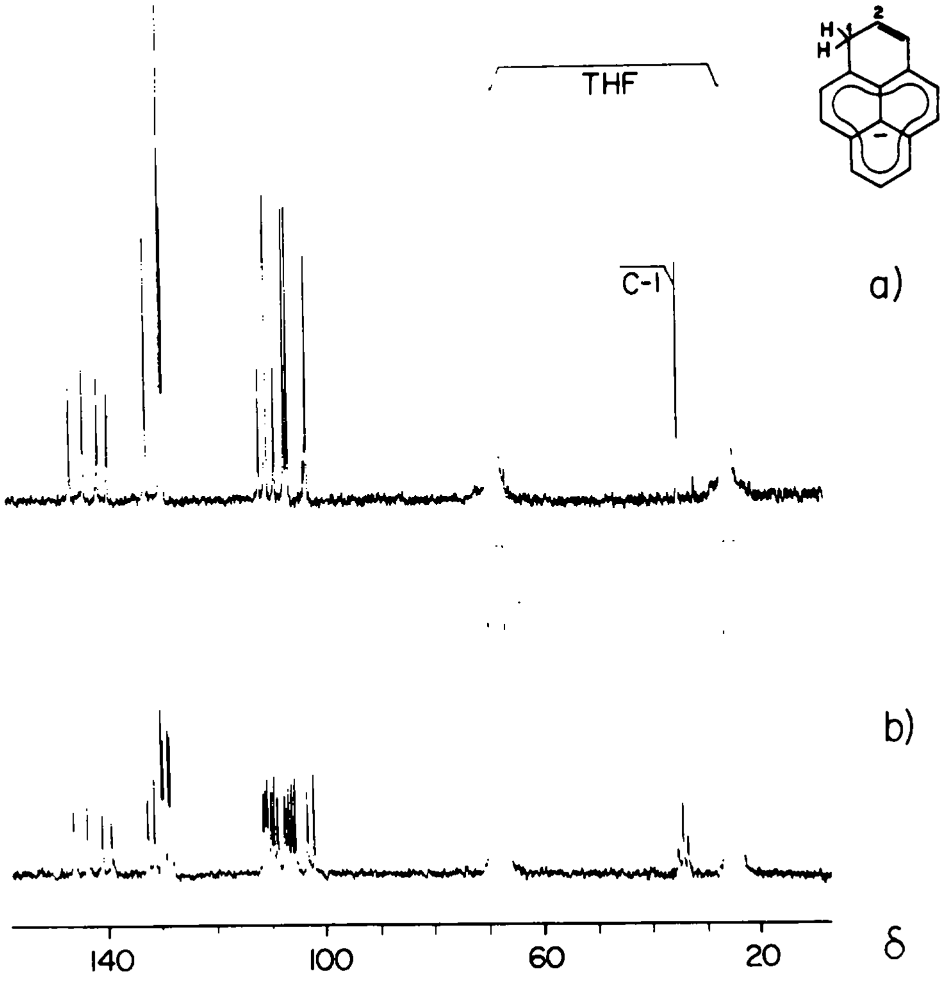


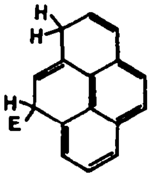
Figure 5. ^{13}C NMR spectra [75.5 MHz, THF/NH_3 5:1, -40°C; a) decoupled, b) non-decoupled] of $(\underline{1}\text{-H})^-/Li^+$.

3.2. Understanding the Reductive Alkylation of Pyrene.

It is clear that the reaction of the ionic pyrene systems with electrophiles can only be rationalized satisfactorily on the basis of the above structural findings. This is true for the number of electrophiles being incorporated and for the regioselectivity of the reaction.[21]

Given the formation of both the pyrene dianion and the monoanion (1-H)$^-$ upon the sodium reduction in etheral solvents it is not surprising that both mono- and dicarboxylic acids are produced upon carbonization.[22] The situation is totally different in liquid ammonia where only the monoanion (1-H)$^-$ exists. This reaction will lead to the attack of only one electrophile E$^+$ if the neutral product 1-H,E, thus, formed is not subsequently reconverted into a monoanion by reaction with base.[23,24]

1-H,E



Turning to the question of regioselectivity, it is generally accepted that the kinetically controlled attack of the electrophile upon the ionic π-system proceeds at the position of the highest π-charge. It is reasonable that the protonation of 1^{2-} affords the monoanion (1-H)$^-$ since the positions 1,3,6 and 8 of 1^{2-} are known from the ^{13}C NMR spectra to adopt the highest π- charge density.[25] The reductive alkylation of pyrene in ammonia, however, is not determined by the properties of the dianion, but by those of the monoanion (1-H)$^-$ which has already accepted a proton as first electrophile! Thus, there is no need to invoke a dianion structure such as $(1^{2-})^*$ in order to rationalize the preparative findings relating to the formation of 1-H,E.[24]

3.3. The π-Bonding in the Dianion 1^{2-}.

The spectroscopic evidence accumulated above permits a coherent description of the electronic structure of the dianion. Both the sequence of the individual ^{13}C resonances of 1^{2-} (see Table) and the ESR hyperfine coupling constants of $1^{\cdot-}$ can be rationalized by a double or single occupancy of the pyrene LUMO. We will not enter into a detailed discussion of the π-charge and spin density distribution since this has been done on other occasions.[5,11] Focussing on the low field resonances of C-2(C-7) and C-3b(C-5b), however, we point out that the relevant π-MO possesses a nodal plane through the central ethylene moiety. The dianion can, therefore, be looked at as a (16=4n) π-perimeter system with an ethylene bridge. This view is nicely supported by the pronounced paratropism of 1^{2-} which can be inferred from the resonances of the ring protons at very high field (much higher than expected from the pure charge-effect). Under the reasonable assumption that the Li counterions are situated above the π-system they should experience a pronounced deshielding as a consequence of the paratropism of 1^{2-}.[26] The resonance of ^{7}Li at very low field is in full accord with this expectation.

4. Conclusions

4. Conclusions - Pyrene appears as a most suitable subject for delineating the scope and limitations of the alkali metal reduction of unsaturated hydrocarbons. The charged π - systems not only function as electron storage systems with intact molecular framework, but, under particular conditions, also undergo side reactions such as protonation or solvent incorporation. These features together with the occurrence of rapid intermolecular electron exchange processes severely inhibit the structural assignments and the preparative use of the ions. Careful control of the experimental conditions is essential in order to avoid confusions and misinterpretations.

5. Experimental

5.1. Reductions.

Pyrene (1) is recrystallized twice from ethanol prior to use. 2,7-Dimethylpyrene (2) is prepared according to literature procedures.[27]

For the reductions pyrene is placed at the bottom of an NMR or ESR tube and dry solvent distilled in from a storage vessel in vacuo. After the solution has been degassed by repeated freeze and thaw cycles the alkali metals are inserted, deposited in the upper part of the tubes and the tubes sealed. Lithium is brought in under vacuum by a specially constructed press, sodium and potassium via sublimation from a side arm. Ammonia is dried over alkali metal prior to use. In order to avoid even traces of water a carefully dried, evacuated glass cell is sealed which contains the neutral compound and the metal at the bottom and top, respectively, of an NMR tube as well as a side arm with a THF solution of 1^{2-}. The solvent is then transferred by distillation and the NMR tube sealed off.

The NMR measurements have been performed at 300 (^{1}H), 75.5 (^{13}C) and 116.6 (^{7}Li) MHz on a Bruker WM 300 spectrometer. ^{1}H NMR measurements of $(4\text{-}D_8)^-/Li^+$ have also been recorded at 400 MHz. The lock signal is taken from the deuterated solvents. ^{1}H and ^{13}C chemical shifts are measured with respect to the solvent signals and referred to the TMS standard by appropriate increments. ^{7}Li chemical shifts are given with respect to the signal of LiCl (H_2O, 1M) as external reference. Thereby, the 5 mm sample tube is put into an outer 8 mm tube containing LiCl/H_2O.

Preparative reduction experiments are performed in evacuated glass ampoules. The latter contain two compartments. After the reduction experiment has been run in one of them, the solution is separated from the metal by pouring it into the second container in which one performs the quenching reaction.

The ESR spectroscopic measurements have been performed on a Varian E-9 spectrometer. The apparatus used in the photolytic experiments has been constructed according to Fischer and Paul.[28]

5.2. Preparation of $4^-/Li^+$ and 5. A solution of 1 (400 mg, 2 mM) in 10 ml of dry, absolute THF in a sealed glass ampoule is contacted at -78°C with freshly pressed lithium wire. After 12 h the deep blue solution of the dianion is separated from the metal and allowed to stand at room temperature for another 12 h. Thereby the colour changes to deep red and $4^-/Li^+$ is formed. The ampoule is opened and the solution added dropwise to vigorously stirred methanol (2 ml, -78°C) under an argon atmosphere. Upon addition, the colour of the solution fades away instantaneously. After evaporation of the solvent one adds 680 mg (3 mM) of DDQ in 50 ml of absolute toluene to the residue and allows the mixture to reflux for 1 h. After filtration and evaporation of the solvent the residue is chromatographed (aluminium oxide, neutr., act. II-III, methylene chloride). After recrystallization from hexane one obtains 5 as colourless needles. Yield 280 mg (52%), m.p. 60°C. High resolution mass spectrum, calcd. for $C_{20}H_{18}O$ 274.1358; found 274.1356. The NMR spectroscopic description of 5 is given in the Table.

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